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125. POLYMERIZABLE LANGMUIR-BLODGETT MULTILAYERS: THE DEPENDENCE OF PROPERTIES AND HOMOGENEITY ON SUPPORT MATERIALS AND LIPIDS. A. Laschewsky, H. Ringsdorf, Inst. of Org. Chem., University of Mainz, D-6500 Mainz, FRG

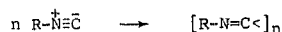
Recently Langmuir-Blodgett multilayers offer an unique combination of well defined order and molecular dimensions. For all potential applications, stability and perfection of the multilayer films is required. This stability is achieved by the polymerization of reactive groups within the amphiphiles. However, the homogeneity of the coating is a severe problem. The quality of the films obtained has been investigated in relation to the support material, the lipid used and the polyreaction. A variety of hydrophobic polymers has been used as supports. The dependence of the quality of the coating on chemical nature, the surface structure and the porosity of the materials was investigated. Different lipids have been studied in an attempt to correlate the behavior with the structure of the head groups. The necessary stabilization of the multilayers via polyreactions induces structural changes within the layers. This can disturb the order of the films or even cause defects. Results for a variety of polymerizable groups such as dienes, diynes or acrylates will be presented.

126. POLYMERIZABLE AMPHIPHILES WITH FLUORINATED CHAINS: FORMATION AND APPLICATIONS OF PHASE-SEPARATED POLYMERIC MIXED MEMBRANES, R. Elbert, T. Folda, H. Ringsdorf, Inst. Organ. Chem., University of Mainz, D-6500 Mainz/FRG

Biomembrane models consisting of two components exhibit either mixing or non-mixing behavior. Mixed membranes from hydrocarbon and fluorocarbon amphiphiles often show phase separation. Using polymerizable and nonpolymerizable lipids, a differentiation between stabilizing and functionalizing arrays in monolayers and liposomes is achieved. The polymeric parts act as a skeleton which stabilizes the functionalized monomeric arrays. They remain accessible to chemical and physical manipulations. The polymer skeleton can be built from either the hydrocarbon or from the fluorocarbon amphiphiles. The use of cleavable, non-polymerizable amphiphile in such a polymeric phase-separated system allows solubilization of non-polymerized portions of the membrane, and thus enables the formation of defined pores in liposomes. The liposomal structure is preserved after the opening reaction. The polymer matrix is essential for retaining the pore structure. In this way, a controlled release of encapsulated materials such as dyes or drugs is possible.

127. POLYMERIZED VESICLES DERIVED FROM ISOCYANO AMPHIPHILES. R.J.M. Nolte. Laboratory of Organic Chemistry, University of Utrecht, Croesestraat 79, 3522 AD Utrecht, The Netherlands.

Double-chain amphiphiles have been synthesized which contain one or two polymerizable isocyano functions. Depending on the type of amphiphile and the experimental conditions, these molecules are able to form closed vesicles when they are dispersed in water. On addition of nickel capronate polymerization occurs of the isocyano functions of the amphiphiles:



This polymerization causes cross-linking of the bilayers and leads to enhanced stability of the vesicle system. The closed vesicles are currently under investigation as models of biomembranes. Channeltype ionophores have been synthesized and incorporated into the bilayers of the polymerized and unpolymerized vesicles. These ionophores are able to bind ions and to mediate their transport across the bilayer membrane.

WEDNESDAY MORNING - SECTION B - ACS AWARD FOR CREATIVE INVENTION SYMPOSIUM HONORING  
R. MILKOVICH (CONTINUED) - J.E. McGrath, Presiding

128. RETROSPECT ON THE DEVELOPMENT OF BLOCK COPOLYMERS. Maurice Morton, Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

Block copolymers are distinguished from graft copolymers only in that the two, or more, separate polymer segments are connected only at the chain ends. However, the physical properties of these two types of polymers, either as heterophase materials or as dispersing agents, may not be greatly influenced by whether they are blocks or grafts. It is only when the block size and distribution can be closely controlled, as in the case of anionic polymerization, that the remarkable properties of block copolymers become evident. This permits the development of useful structure-property relationships, as has been done in the case of the thermoplastic elastomers.

129. S/I DIBLOCK MACROMER GRAFT COPOLYMER SYNTHESIS AND PROPERTIES. G. O. Schultz and R. Milkovich, 5022 Hearthsides Lane, Racine, Wisconsin 53402.

Polystyrene/polyisoprene graft copolymers with structures analogous to SIS block polymers were prepared by free radical copolymerization of styrene monomer with methacrylate-terminated polystyrene-polyisoprene diblock Macromer (SI0125MA) in aqueous suspension. The molded copolymers possessed clarity, impact strengths, and flexural moduli roughly equivalent to those of commercial transparent high impact strength S/B resins prepared by anionic polymerization. Phase separation occurring during the course of polymerization led to the presence of much unreacted Macromer in the product. However, tapered block Macromers having a short polystyrene block separating the polyisoprene block from the methacrylate end group eliminated the terminal phase separation affecting the copolymerization. These tapered block Macromers attained complete conversions.

130. MECHANISM OF RARE EARTH CATALYSIS IN COORDINATION POLYMERIZATION. H. L. Hsieh, Phillips Petroleum Company, Research and Development, Bartlesville, OK 74004.

The microstructure and stereospecificity of a variety of 1,3-diene polymers prepared with lanthanide coordination catalysts were examined. In contrast to the conventional d-orbital transition metal catalysts, the lanthanide catalysts would polymerize 1,3-diene monomers prevailingly in a 1,4-addition manner. The cis and trans 1,4-stereoregular polymerizations depend on the steric and electronic structures of the dienes. Under the same lanthanide catalysts the 1,4-dimethyl butadiene (e.g. trans-trans-2,4-hexadiene) leads exclusively to trans-1,4 polymer, the 2,3-dimethyl butadiene gives mainly cis-1,4 polymer, whereas the 1,3-dimethyl butadiene (e.g. trans-2-methyl-1,3-pentadiene) produces mixed trans/cis (60/40) 1,4-polymers. The ligands in the lanthanide catalyst and the polymerization conditions have relatively little effect on the stereoregulation. It is proposed that the polymerization mechanism involves the bidentate coordination of the diene monomer through both double bonds in the cisoid conformation, followed by an anti-syn isomerization of the growing allylic unit at the moment of monomer insertion. The rate of anti-syn isomerization is affected by the structure of the monomer.

131. INVESTIGATIONS OF DIFUNCTIONAL ORGANOLITHIUM INITIATORS. A. D. Broske and J. E. McGrath, Department of Chemistry and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

The dianionic species prepared from the addition of two moles of sec-butyl lithium to one mole of the diene 1,3 bis(phenyl ethenyl) benzene produces a difunctional organo-lithium initiator which is both soluble in hydrocarbon media such as cyclohexane and has sufficient thermal stability. The kinetics of this reaction can be followed by UV/ visible spectroscopy and gas liquid chromatography. Spectroscopic results indicate an energy of activation of 18.8K cal/mole for this addition which is comparable to other anionic initiation reactions. Chromatographic data strongly suggests a consecutive reaction mechanism and that the two double bonds are not completely isoreactive in